

Crystalline sodium or potassium silicon titanates prepared at temperatures of 200 °C or less as catalysts supports

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## 1. INTRODUCTION

Hydrous sodium or potassium titanium and hydrous titanium/silicon oxides have been shown to be excellent precursors in the preparation of active hydrogenation catalysts (1,2,3,4). Anthony and Dosch (5) and Anthony et al. (6) recently reported the synthesis of six new layered crystalline titanates, and the catalytic activity of Pd and sulfided NiMo supported on these titanates. TS-1, a titanium-silicalite, is a mild oxidation catalyst for epoxidation of olefins and hydroxylation of phenols and aromatics when using hydrogen peroxide as the oxidant. Zorite, a natural molecular sieve with a Si/Ti ratio of 2.6, has been synthesized by Kuznicki, USP 4,853,202. He has also synthesized molecular sieves with Si/Ti ratios in the range of 2 to 10. Young, USP 3,329,481 synthesized a Si/Ti compound (TS 26), which he called a molecular sieve, but the XRD pattern is characteristic of a layered material.

This manuscript reports the synthesis and catalytic activity of sodium and potassium silicon titanates when used as precursors in preparation of sulfided NiMo catalysts. Catalytic activity is determined by using the model reactions, hydrogenation of pyrene at 300 °C and hydrodesulfurization of dibenzothiophene at 350 °C. Stephens et al. (7,8,9) have shown that rate constants for pyrene hydrogenation correlate with ultimate catalytic activity for coal liquefaction.

## 2. EXPERIMENTAL

The chemicals used in the preparation of a sodium silicon titanate (TAM-1) and a potassium silicon titanate (TAM-4) were tetraisopropyl orthotitanate, tetraethyl orthosilicate, an aqueous solution of sodium hydroxide, an aqueous solution of potassium hydroxide, a solution of tetramethylammonium hydroxide (TMAOH) in methanol, and tetraalkylammonium bromide (TRAB), where the alkyl group, R, was propyl, butyl or pentyl. The synthesis procedure was in two parts. First, an aqueous mixture containing all the reagents except the alkoxides was prepared. Second, the alkoxides were mixed and then added to the aqueous mixture while stirring and a gel formed. These ingredients were transferred to a reactor, which was placed in an oven preset to the appropriate temperature. Reaction times were 90 to 96 hours. The sodium silicon titanate was recovered by filtration and washing the precipitate with water and acetone. Typical molar ratios of Na or K:TMAOH:H<sub>2</sub>O:MeOH:TPAB:Si:Ti were 1:1.58:200:13:3:1:1 for TAM-1 and 2:0:175:0:2:1:1 for TAM-4. The procedure for preparing the sulfided nickel catalyst was the same as for the T2CT as reported by Anthony et al (6).

Activity experiments were conducted in minibatch reactors at 300 °C and 350 °C for pyrene hydrogenation and for hydrodesulfurization (HDS), respectively. The reactors were charged with 10 mg of catalysts, a solution containing 10% pyrene in hexadecane, and hydrogen pressure of 1000 psi at room temperature. The minibatch reactors were immersed in a constant temperature fluidized sand bath for a period of 15 minutes. After reaction the reactors were quenched, and the products were analyzed by gas chromatography. A similar procedure was followed for the HDS experiments, except dibenzothiophene was used instead of pyrene.

### 3. RESULTS AND DISCUSSION

#### 3.1 Catalyst Characterization

The XRD patterns for TAM-1 and TAM-4 are presented in Figures 1 and 2. TAM-1 had the following properties: The first peak of the XRD was at  $d_0$ -spacings of 1.47-1.5 nm. Other properties were surface areas of 150 to 170 m<sup>2</sup>/g, pore volumes of 0.9 to 1.0 cc/g, and a weight loss of 18 to 20% on heating for 10 hours in a vacuum at 170 °C. Weight loss on heating to 500 °C varied from 15 to 20% as compared to the 35 to 40% observed for TAM-4 and T2CT (6,7). The peaks at  $d_0$ -spacings of 5.4, 5.2, 3.71 and 3.60 nm disappeared after evacuation for 10 hours at 170 °C. The FTIR spectra shown in Figure 3 for TAM-1 has distinct peaks, a doublet or W shaped peaks in the range of 830 to 1020 cm<sup>-1</sup>. The relative intensities of the peaks at 1490 cm<sup>-1</sup> and 1640 cm<sup>-1</sup> are greater when tetrabutyl ammonium bromide is used in the synthesis compared to those when tetrapropyl ammonium bromide is used. The triplet at 4250 cm<sup>-1</sup> characteristic of quaternary ammonium compounds is present, but the absorption bands due to the primary C-H stretches are absent except when tetrapentyl ammonium bromide is used as the template. The average C:N ratio of  $6 \pm 1.2$  obtained for TAM-1 indicates incorporation of mostly TMAOH even though the TP<sub>3</sub>AB, TBAB, or TP<sub>3</sub>AB was used in the synthesis. When heating TAM-1 from 100 to 500 °C, the differential scanning calorimeter (DSC) recorded exothermic regions with peaks at 260 °C (376 mw/g) and 325 °C (543 mw/g). After heating TAM-1 for four hours at 500 °C or a shorter time at 700 °C, two phases as determined by XRD and electron microscopy characteristic of titania and silica were present.

The ion exchange capacity of TAM-1 was determined by using the following procedure. A 0.1 N HCl solution was to be added to a slurry of 50 mg TAM-1 in 50 ml of distilled, deionized water to maintain a pH of 3 for a period of 4 hours. Then it was filtered and rinsed with water and acetone and air dried. This procedure was repeated for the solids a second time. Eighty two percent of the sodium was removed in the first exchange and 86% of the remaining sodium was removed in the second exchange for a total sodium removal of 97.5 %. Hence, the ion exchange capacity was 4.1 meq/g, which is approximately equal to the initial sodium content (7.9 wt%).

TAM-4 had a  $d_0$ -spacing of 0.78 nm and a distinctly different XRD pattern from TAM-1. The quaternary ammonium compounds were not incorporated into the structure as indicated by the absence of the IR peak at 1490 cm<sup>-1</sup> in the FTIR spectra (Figure 4), and the low nitrogen content (<0.09%) from the CHN analysis. When heated to 500 °C for four hours or more the samples were converted to anatase titania and silica, and the percent volatiles was 40 to 45% (based on room temperature drying). If a sample was dried at 100 °C prior to calcination the volatiles were approximately 20%. TAM-4 was prepared with KOH/Ti ratios of 1.5 to 2.7, and variation of the concentration of the quaternary compounds appeared to have little effect on the XRD patterns of the final material. The DSC for TAM-4 was endothermic over the complete temperature range with a peak at 160 °C (-545 mw/g). Surface area of the as prepared TAM-4 was 194 m<sup>2</sup>/g.

Analysis for titanium and silicon were determined by AA and ICP on selected TAM-1 and TAM-4 samples. The Si/Ti atomic ratios in the products were within 5% of the Si/Ti ratio in the charge solution.

Two U. S. patents (4,938,939, July 3, 1990, and 7,853,202, August 1, 1989) were issued in 1989 and 1990 to S. Kuznicki on the synthesis of small pore and large pore crystalline titanium/silica molecular sieves. These molecular sieves represent new structures with titanium in octahedral coordination and silicon in tetrahedral coordination. The Si/Ti ratios are in the range of 2 to 10 and preferably 5. The XRD patterns and compositions of these molecular sieves are significantly different than the titanates prepared in this study. However, work by Young, USP 3,329,481, claims the synthesis of a titanium silicate molecular sieve, TS-26. Examples presented by Kuznicki on Young's

work are a TS-26/ETS-1 are more fully characterized than the samples synthesized by Young. The bar spectra in Figure 2 is the XRD spectra for ETS-1/TS-26. TAM-4 appears to be a different material than ETS-1/TS-26 since the TAM-4 contains several new peaks, and not all of the remaining peaks match the bar spectra.

A material labelled ETS-2 was also synthesized by Kuznicki, but not claimed in the patent. The same procedure was used as in preparing TS-26, but no potassium was used in the synthesis. Even though the starting mixture contained approximately 1:1 Ti:Si, the material synthesized was "almost devoid of silica," and had significant peaks at 0.875, 0.370 and 0.316 nm with relative intensities of 85, 40, and 100, respectively. Obviously, this material is different than TAM-1 or TAM-4.

### 3.2 Catalytic Activity

A comparison of catalytic activity for hydrogenating pyrene to dihydropyrene using sulfided Ni/Mo supported on T2CT (6), TAM-1, TAM-4, hydrous titanium oxide, and hydrous silicon titanium oxide with the commercial catalysts, Shell 324 and Amocat 1C, is shown in Table 1. The data illustrate that sulfided Ni/Mo supported on T2CT (6), TAM-1, and TAM-4 have comparable activity on an active metal basis as the commercial catalysts and the Ni/Mo- $\text{Na}_{0.5}\text{Ti}$  amorphous catalyst, but the sulfided Ni/Mo  $\text{Na}_{0.5}\text{TiSi}_{0.25}$  amorphous catalyst has a much higher activity. For the amorphous Ti catalysts, as well as, T2CT(6), the majority (>98%) of the sodium was removed prior to loading with Mo and Ni by using 0.1 N HCl. However, TAM-1 and TAM-4 had sodium and potassium levels of 2.27% and 3.61%, respectively, prior to the loading even though ion exchange had been performed. Initial sodium and potassium levels of TAM-1 and TAM-4 varied from 8 to 12%. The ion exchange procedure used to determine the extent of exchange and the procedure used in the catalysts preparation were different. Aqueous mixtures of approximately 10% solids were used when preparing the catalysts instead of the 0.1% solids used in determining ion exchange capacity. Table 1 also illustrates the significant resistance to pore diffusion exhibited by the commercial catalysts.

The HDS activity of the TAM catalysts is shown in Table 1. The catalytic activity of TAM-1 and TAM-4 on a per gram of catalysts is considerably less than that of Shell 324. This difference is probably due to the low molybdenum loading since the activity of the TAM catalysts on a per gram of Mo basis is substantially greater than that for Shell 324. A significant difference occurs in the ratio of biphenyl to cyclohexyl benzene, which is much greater for the TAM catalysts than Shell 324 or the Sandia amorphous catalysts. The ratio also varies significantly for the TAM catalysts depending on the method of preparation.

### 4.0 CONCLUSION

Two new alkali silicon titanates have been synthesized which show high hydrogenation activities when used as precursors for sulfided NiMo catalysts. Based on the XRD patterns these are new materials. Even though the first reflection of TAM-4 and TS-26 and ETS-1 are the same, the remaining portion of the spectra indicates that TAM-4 is a different material. A characteristic of TAM-1 is the doublet that occurs between 830 and 1010  $\text{cm}^{-1}$  on the FTIR. Incorporation of template appears to be indicated by the peak at 1490  $\text{cm}^{-1}$  and the overtone bands at 4250  $\text{cm}^{-1}$ .

### 5. ACKNOWLEDGMENTS

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Table 1. Comparison of Catalysts Activities for Hydrogenation of Pyrene (pyr) and Hydrodesulfurization (HDS) of Dibenzothiophene

| Catalyst  | Form   | Mo, % <sup>a</sup> | Ni, % <sup>a</sup> | SA, m <sup>2</sup> /g <sup>a</sup> | k <sub>pyr</sub><br>(g cat g <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup> | η <sub>pyr, hydo.</sub> | k <sub>HDS</sub><br>(g cat g <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup> | k <sub>HDS</sub><br>(g Mo g <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup> | BP/CHB |
|---|--|--------------------|--------------------|------------------------------------|---|-------------------------|---|--|--------|
| Shell 324   | 1/32" Extrud.  | 13.2               | 2.7                | 152                                | 0.041   | 0.31                    | 0.016   | 0.121  | 1.6    |
| Shell 324   | -100 Mesh  | 13.2               | 2.7                | 152                                | 0.120   | 0.91                    | ND  | ND   | ND     |
| Shell 324   | -200 Mesh  | 13.2               | 2.7                | 152                                | 0.158   | 1.20                    | 0.028   | 0.158  | 1.9    |
| Amocat 1C   | 1/16" Extrud.  | 10.7               | 2.4                | 177                                | 0.038   | 0.36                    | ND  | ND   | ND     |
| Amocat 1C   | -100 Mesh  | 10.7               | 2.4                | 177                                | 0.059   | 0.55                    | ND  | ND   | ND     |
| Amocat 1C   | -200 Mesh  | 10.7               | 2.4                | 177                                | 0.155   | 1.45                    | ND  | ND   | ND     |
| NiMo-Type 2 CT<br>(Batch #50)                       | -100 Mesh<br>Sulfided @ 425 °C                       | 5.35               | 1.76               | 160 <sup>d</sup>                   | 0.065   | 1.22                    | ND  | ND   | ND     |
| TAM-1, S/IT = 1.1                                   | -100 Mesh/calcined<br>@ 500 °C/acidified<br>@ 425 °C | 2.85               | 0.97               | 160 <sup>d</sup>                   | 0.027   | 0.94                    | 0.0085  | 0.30   | 11.9   |
| TAM-1, S/IT = 1.1                                   | -100 Mesh/sulfided<br>@ 425 °C                       | 2.85               | 0.97               | 160 <sup>d</sup>                   | 0.024   | 0.83                    | 0.0073  | 0.26   | 3.16   |
| TAM-4, S/IT = 1.0                                   | -100 Mesh/calcined<br>@ 500 °C/acidified<br>@ 425 °C | 1.93               | 0.65               | 194 <sup>d</sup>                   | 0.025   | 1.30                    | 0.0010  | 0.513  | 12.3   |
| TAM-4, S/IT = 1.0                                   | -100 Mesh/sulfided<br>@ 425 °C                       | 1.93               | 0.65               | 194 <sup>d</sup>                   | 0.026   | 1.36                    | 0.0084  | 0.43   | 8.3    |
| NiMo-Ni <sub>2</sub> Te <sup>h</sup>                | -100 Mesh  | 11.2               | 3.7                | 130                                | 0.186   | 1.66                    | 0.0302  | 0.302  | 2.8    |
| NiMo-Ni <sub>2</sub> Te <sub>1.5</sub> <sup>h</sup> | -100 Mesh  | 8.7                | 3.0                | 166                                | 0.268   | 3.08                    | 0.0132  | 0.985  | 2.8    |

<sup>a</sup>Composition and surface areas of as-received Amocat 1C and Shell 324. Composition of HTO and CT-based Catalysts after calcination @ 500°C. <sup>b</sup> These are the latest and best of the HTO-Based NiMo Catalysts. <sup>c</sup>Prior to ion exchange and after degassing at 150 °C for 12 hours. <sup>d</sup> Effectiveness Factor; Effective Diffusivities based on pyrene for Shell 324 and Amocat 1C are 6.5 (10)<sup>-12</sup> and 3.2 (10)<sup>-11</sup> m<sup>2</sup>/s. The effectiveness factors were calculated assuming a pseudo first order rate equation and spherical particles. <sup>e</sup>Calculated based on an estimate of the effective diffusivity of pyrene. ND Not determined. BP/CHB Moles of biphenyl divided by the moles of cyclohexyl benzene. A high ratio indicates efficient utilization of hydrogen.

## 6. LITERATURE CITED

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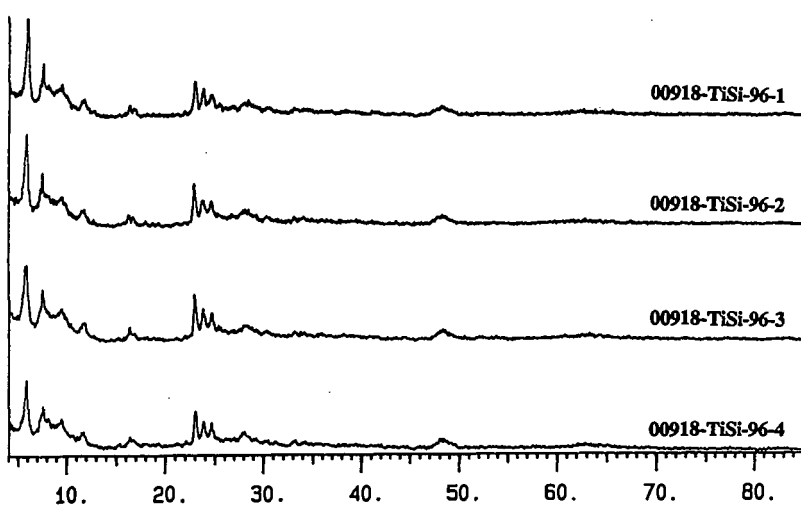


Figure 1. Comparison of XRD Patterns for TAM-1 Prepared with Different Charge Compositions.

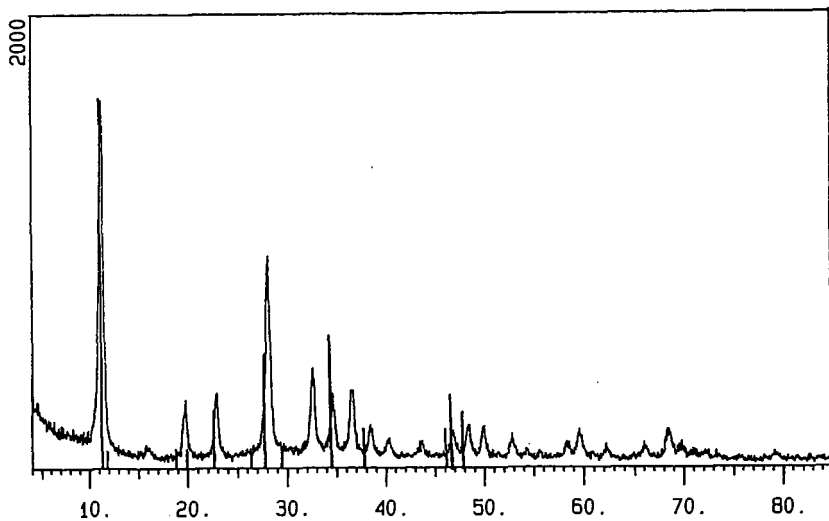


Figure 2. Comparison of XRD Powder Patterns for TAM-4 and ETS-1/TS-26 (Bars).

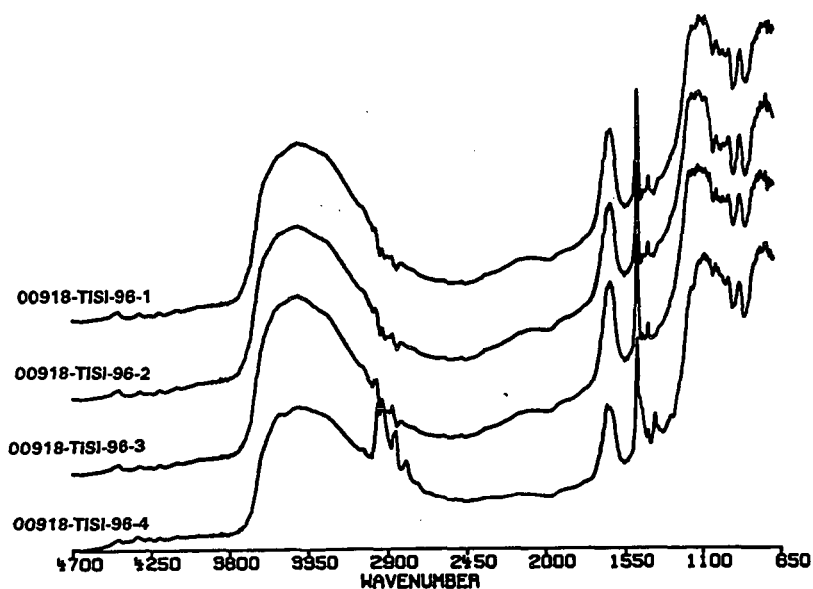


Figure 3. Comparison of FT-IR Spectra for TAM-1 Prepared Using TP<sub>3</sub>AB and TP<sub>5</sub>AB.

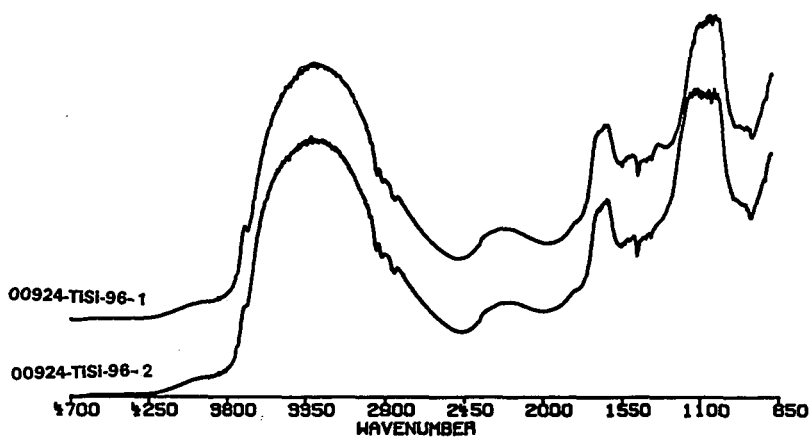


Figure 4. Comparison of FT-IR Spectra for Different Batches of TAM-4.